Quantum transport through single-molecule junctions with orbital degeneracies

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(Dated: April 12, 2010)

We consider electronic transport through a single-molecule junction where the molecule has a degenerate spectrum. Unlike previous transport models, and theories a rate-equations description is no longer possible, and the quantum coherences between degenerate states have to be taken into account. We present the derivation and application of a master equation that describes the system in the weak-coupling limit and give an in-depth discussion of the parameter regimes and the new phenomena due to coherent on-site dynamics.

I. INTRODUCTION

The field of molecular electronics has greatly benefited from the possibility of formulating transport problems in the weak-coupling regime as rate equations for sequential tunneling processes.[1–9] Given the spectrum of the molecule and the tunneling-matrix elements, the different features of the steady-state current–voltage characteristics can immediately be mapped onto the energetic availability or non-availability of certain jump processes. Rate equations are the Markovian kinetic equations for the lowest-order expansion of the von Neumann equation with respect to the tunneling Hamiltonian while neglecting any off-diagonal elements of the reduced density matrix. Such an approximation is well justified for non-degenerate systems, when the differences of the molecular eigenenergies are much larger than any tunneling-induced level shift or broadening. As molecules often feature geometric and thus orbital symmetries, the system Hamiltonian of a single-molecule junction shows degenerate levels. Due to the quantum-mechanical nature of the tunnel junction, the rate-equation description is in general inadequate for these systems.

The problem of electronic transport through quantum nanostructures with degenerate levels has already been given some attention in different parts of the literature. The comprehensive review of Markovian master equations by Timm[10] shows the equivalence of different methods and approaches used to derive master equations for weak-coupling problems. In Refs. 11 and 12, the coupling of a spin-degenerate quantum dot to ferromagnetic leads causes coherent dynamics described by the full master equation which significantly differ from the spectroscopic picture found in rate-equation treatments. The problem of using the rate-equation formalism for molecules with orbital symmetries has already been addressed in our previous study on Jahn–Teller molecules.[13] An implementation of the full master-equation formalism for a genuine molecular-electronics problem is discussed in Refs. 14 and 15, however, only for a very special and rather complex type of molecule.

The dynamics of a master equation[30] is, in contrast to a rate equation, much less intuitive as the tunneling elec-

trons are allowed to jump into and out of linear superpositions of the degenerate molecular states. The coupling to the continuum of states in the electronic reservoirs via virtual transitions generates an intrinsic dynamics on the molecule that is not related to real changes of the number of electrons in the system. The image of the dynamics as a succession of well-defined quantum jumps between the leads and the molecule, which renders the rate equation so simple in its use and tempting for application, is declared void by the quantum mechanical nature of the degenerate system.

The basic phenomenology of quantum transport through nanostructures with orbital degeneracies in the absence of vibrations and in particular the proper derivation of a Markovian master equation for the treatment of near-degeneracies has already been investigated by us in Ref. 16. There we establish the "decoupling paradigm", which states that for generic tunnel amplitudes, there is always a basis of the molecular Hilbert space where one of the (near-)degenerate levels is decoupled from the drain electrode. Below the double-charging threshold, this level is rendered a dark state in which charge is accumulated, and electronic transport across the nanostructure is strongly inhibited. This coherent current-blockade is only partially lifted due to the tunneling-induced renormalization of the isolated structure's levels, as by transitions via virtual intermediate states in the source electrode, the electron is moved out of the dark state and allowed to tunnel to the drain electrode. A particularly appealing interpretation of this dynamics uses the picture of a pseudo-spin and the tunneling-induced renormalization as a pseudomagnetic field acting on that pseudo-spin.[11]

The purpose of this article is the extension and discussion of the model to single-molecule devices, mainly the relation of the physics caused by the orbital degeneracies to the vibronic dynamics of the molecular cage. After having defined the most general model of a linear electron–phonon coupling, we shall show that for the study of degenerate systems this can be reduced to two genuinely different types of molecular models, which significantly differ in their transport properties. One of them, which we shall term "Anderson–Holstein model",

will simply show a superposition of a vibronic sideband structure and the already known coherent current blockade generic for degenerate electronic systems. The ratio of charging energy to vibronic energy will be shown to characterize the steady-state current–voltage profile: for large charging energy, the vibronic sidebands will appear as peaks instead of steps and thus render the appearance of negative differential conductance a generic property of single-molecule junctions with degenerate orbitals. The other, a Jahn–Teller active model, will show a strong dependence of the electronic transport properties on the coupling to the leads.

In the last section, we shall extend the basic model incorporate elements that are related to possible experimental issues including the modifications of the transport properties due to slight breaking of the orbital degeneracy, general linear electron–phonon coupling, and the presence of many modes in the electronic reservoirs.

Not surprisingly, our results will reproduce certain effects and features, which have already been reported by several groups;[11,14,15,17] what we, however, do want to show is that by using a bottom-up approach and adding complexity to the models in several steps, we succeed in tracing the fundamental and generic physics back to the intrinsic properties of the master equation and are thus in a much better position to actually apply the theory to experiments.

II. GENERAL PROPERTIES OF THE HAMILTONIAN

The model of a single-molecule junction, as we consider it in this article, consists of three parts: the single molecule itself, H_{mol}, the source and the drain electrodes through which electrons are injected and extracted, H_{leads}, and a tunnel-coupling between the two, H_T. The electrodes, α being an index for left and right, are modeled as spinless, non-interacting Fermi gases, $H_{leads} = \sum_{k\alpha} \varepsilon_k c^\dagger_{k\alpha} c_{k\alpha}$, in the wide-band limit, that is with constant density-of-states ν_0. The molecule, in order to distinguish it from quantum dot systems, is a discrete electronic system coupled to a single vibrational mode.[1,4,18] The electronic part in our model is rather simple. We consider two degenerate levels that can be detuned from their energy ε_0 by the gate-voltage of the molecular junction, a Coulomb interaction of strength U between the two, but no intra-molecular tunneling. A small energy difference between the two levels of the order of the tunneling-induced level shift can easily be included in the model and the thus resulting derivation of the master equation by application of the singular-coupling limit,[16] modifies the equation only marginally; we shall return to this later in section IV A. The molecular vibrations are modeled as a harmonic oscillator of frequency ω being coupled to the electronic degrees of freedom by $H_{el–ph}$ specified in the next section. The

Hamiltonian of the molecule is thus

$$H_{mol} = (\varepsilon_0 + eV_g)(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow + \hbar\omega b^\dagger b + H_{el–ph}. \quad (1)$$

The two degenerate electronic levels are, in analogy to the notation of spin, labeled $|\uparrow\rangle$ and $|\downarrow\rangle$. In case we have to sum over the different levels, we switch to denoting the levels by $|\sigma\rangle$ and its opposite $|\bar\sigma\rangle$. The tunneling part, where from the beginning, we assume the amplitudes $t_{\alpha\sigma}$ to be independent of the electrons' wave vector, is

$$H_T = \sum_{k\alpha\sigma} t_{\alpha\sigma} c^\dagger_{k\alpha} d_\sigma + \text{h.c.} \quad (2)$$

For notational convenience, we define a coupling tupel $\boldsymbol{\Gamma} := (\Gamma_{L\uparrow}, \Gamma_{L\downarrow}, \Gamma_{R\uparrow}, \Gamma_{R\downarrow})$ being derived from the respective Golden-Rule expressions $\Gamma_{\alpha\sigma} := \frac{2\pi}{\hbar}\nu_0 |t_{\alpha\sigma}|^2$.

A. Electron–Phonon coupling and Degeneracies

The general form of a linear coupling of the oscillator's coordinate to the charge number of a degenerate two-orbital molecule is

$$H_{el–ph} = \hbar\omega \sum_{\sigma,\tau=\uparrow,\downarrow} \lambda_{\sigma\tau} d^\dagger_\sigma d_\tau (b^\dagger + b). \quad (3)$$

When the expression for $H_{el–ph}$ is diagonalized in the space of degenerate electronic levels, which is necessary for the derivation of the master equation, the only non-trivial couplings are those to the excess charge and the charge difference, respectively,

$$H_{el–ph} = \lambda\hbar(b^\dagger + b)\big(\lambda_0(n_\uparrow + n_\downarrow) + \lambda_z(n_\uparrow - n_\downarrow)\big). \quad (4)$$

The canonical transformation generally used to eliminate the electron–phonon coupling—the polaron transformation[19]—induces a renormalization of the electronic eigenenergies—the polaron shift—which is proportional to the square of the electron–phonon coupling strength. The energy of the state $|\uparrow\rangle$ will thus be renormalized by $(\lambda_0 + \lambda_z)^2 \hbar\omega$ and the one of $|\downarrow\rangle$ by $(\lambda_0 - \lambda_z)^2 \hbar\omega$, accordingly. The Hamiltonian in the polaron picture is, however, the starting point for the perturbative analysis of the von Neumann equation, and the question, whether we deal with a degenerate, a near-degenerate, or a non-degenerate system refers to this picture and the renormalized energies thereof. In case the electron–phonon coupling is assumed to be sufficiently strong, such that the polaron shift is much larger than the tunneling-induced broadening Γ, the system is effectively non-degenerate, and the canonical rate-equation formalism can be applied. If the polaron shift is of the order Γ, the electronic term has to be treated in the singular-coupling limit,[16] which will be touched briefly in section IV A. For the setting with strictly degenerate orbitals that we wish to discuss here, the polaron shift of both levels has to be equal, which limits the possible choices of the electron–phonon

coupling in the above expression to either λ_0 or λ_z being zero. For strictly degenerate systems, we thus assume, without loss of generality,

$$H_{\text{el-ph}} = \lambda\hbar\omega(b^\dagger + b)(n_\uparrow \pm n_\downarrow). \qquad (5)$$

Choosing the plus sign, we obtain a trivial generalization of the single-mode Anderson–Holstein Hamiltonian.[20] This choice is therefore termed the "Anderson–Holstein molecule". The minus sign, on the contrary, makes the electron-phonon coupling that of an $E \otimes b$ Jahn–Teller effect.[21,22] We call this model the "Jahn–Teller molecule". Certain transport properties of Jahn–Teller systems in the rate-equation regime are analyzed in Ref. 13. By absorbing the sign into orbital specific electron–phonon couplings λ_σ, the Anderson–Holstein molecule is defined by $\lambda_\uparrow = \lambda_\downarrow$, whereas the Jahn–Teller case is given when $\lambda_\uparrow = -\lambda_\downarrow$.

The polaron transformation renormalizes not only the single-particle energy $\varepsilon_0 \mapsto \varepsilon_0 - \lambda^2\hbar\omega$ but also the charging energy $U \mapsto U - 2\,\text{sgn}(\lambda_\uparrow\lambda_\downarrow)\hbar\omega$. As in the Jahn–Teller case, both orbitals are shifted to opposite directions, occupying such a molecule with two electrons will result in a zero net shift of the adiabatic potential, see Figure 1. The renormalization of the charging energy U will therefore be positive; in contrast to the Anderson–Holstein model, the Jahn–Teller molecule induces a repulsive interaction between the two electrons in the polaron picture, not an attractive one.[23]

B.   Existence of Dark States

As we already know from the treatment of purely electronic structures,[16] the master equation can be understood best in a coordinate system of the degenerate levels, in which one of them is decoupled from the drain electrode. Then a dark state is formed and causes the stationary current to be strongly suppressed. In the polaron picture, where the tunnel amplitudes are matrix valued, this property is modified. Consider first the case without electron–phonon coupling. We apply a unitary transformation in the two-dimensional complex vector space $\mathcal{H}_{\text{el}}$ spanned by the operators $d_\uparrow$ and $d_\downarrow$,

$$\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} := \begin{pmatrix} \cos\theta & e^{\imath\varphi}\sin\theta \\ -e^{-\imath\varphi}\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} d_\uparrow \\ d_\downarrow \end{pmatrix}. \qquad (6)$$

All parts of the Hamiltonian except the tunneling term are invariant under this transformation. The tunneling Hamiltonian becomes

$$\tilde{H}_T = \sum_{\boldsymbol{k}\alpha} c_{\boldsymbol{k}\alpha}^\dagger \big((t_{\alpha\uparrow}\cos\theta + t_{\alpha\downarrow}e^{\imath\varphi}\sin\theta)d_1$$
$$+ (t_{\alpha\downarrow}\cos\theta - t_{\alpha\uparrow}e^{-\imath\varphi}\sin\theta)d_2\big) + \text{h.c.} \qquad (7)$$

By choosing suitable angles θ and φ, the second term of one of the above equation vanishes for at least one electrode, allowing the formation of a dark state: the

basis of the coherent current blockade as we have explained in Ref. 16. Under certain circumstances, that is for specific choices of the tunnel-couplings, the Hamiltonian can be further simplified. If the condition $t_{\alpha\downarrow}\cos\theta = t_{\alpha\uparrow}e^{-\imath\varphi}\sin\theta$ can be fulfilled for *every* α, the second term in Eq. (7) will vanish completely and the system will only couple the state d_1 to the electrodes, thus reducing it to an effective single-level system with tunneling matrix elements $|t_\alpha^{\text{eff}}|^2 = |t_{\alpha\uparrow}|^2 + |t_{\alpha\downarrow}|^2$. This condition reads

$$\varphi = \arg\frac{t_{\alpha\uparrow}}{t_{\alpha\downarrow}} \quad \text{and} \quad \theta = \arctan\frac{|t_{\alpha\downarrow}|}{|t_{\alpha\uparrow}|}, \qquad (8)$$

for all α. In the following, we shall assume real $t_{\alpha\sigma}$ for simplicity and accordingly set $\varphi = 0$.

1.   Anderson–Holstein

In the case of phonons, we have to distinguish the Anderson–Holstein and the Jahn–Teller case. In the polaron picture where the tunnel amplitudes are matrix-valued $t_{\alpha\sigma} \mapsto t_{\alpha\sigma}e^{-\lambda_\sigma(b^\dagger - b)}$, the second term of Eq. (7) reads for electrode α

$$c_{\boldsymbol{k}\alpha}^\dagger t_{\alpha\downarrow}\cos\theta(e^{-\lambda_\downarrow(b^\dagger - b)} - e^{-\lambda_\uparrow(b^\dagger - b)})d_2. \qquad (9)$$

The electron-phonon coupling of the Anderson–Holstein molecule is characterized by the condition $\lambda_\uparrow = \lambda_\downarrow$ thus rendering the term (9) zero. In this model, the decoupling paradigm and the emergence of a dark state works the same way as for purely electronic levels. In the decoupling regime, such a molecule is equivalent to a single-level molecule. The Jahn–Teller molecule, however, has $\lambda_\uparrow = -\lambda_\downarrow$ making a detailed discussion of the transition rates necessary.

2.   Jahn–Teller

Transforming the molecular Hamiltonian into the polaron picture essentially consists of shifting the adiabatic potential of the oscillator by $\sqrt{2}\lambda_\sigma\ell_{\text{osc}}$. The Franck–Condon matrix element $M_\sigma^{qq'} = |\langle q | e^{-\lambda_\sigma(b^\dagger - b)} | q'\rangle|^2$ at row q' and column q itself is the overlap of the original vibrational state $|q\rangle$ with the shifted oscillator's state $|q'\rangle$. The modulus of the matrix elements is independent of the direction of the shift, the sign, however, is not. A transition between states that both have an even or odd number of excited quanta still is independent of the direction. A transition from a state with an even number of quanta to one with an odd number of quanta, however, is sensitive to the direction. In the matrix $e^{\lambda(b^\dagger - b)} - e^{-\lambda(b^\dagger - b)}$, only the matrix elements belonging to excitations of an even number of oscillator quanta cancel. In the pre-factor of d_1, the matrix $t_{\alpha\uparrow}\cos\theta e^{-\lambda(b^\dagger - b)} + t_{\alpha\downarrow}\sin\theta e^{\lambda(b^\dagger - b)}$, however, there are no cancellations to be expected. Only in the case of equal coupling, $t_{\alpha\sigma} = 1$ for all α and σ,
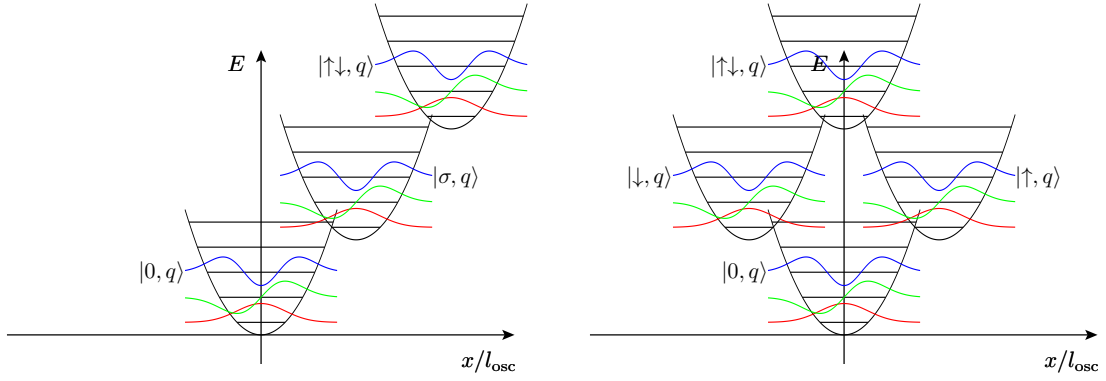
FIG. 1: Adiabatic potentials of the Anderson–Holstein molecule (left) and the Jahn–Teller molecule (right). The first few vibronic wavefunctions are indicated in order to see the direction dependence of their overlap in the Jahn–Teller case.

the matrix elements for excitations of an odd number of quanta cancel. In that special case, the Hamiltonian couples transitions with $|q - q'|$ even to d_2 and transitions with $|q - q'|$ odd to d_1. Since the both subsets of transitions change the oscillator's energy by either even or odd multiples of $\hbar\omega$, only, the system decouples into two independent subsystems with disjoint spectra, which in the weak-coupling limit can be treated by rate equations. As simple and tempting a treatment by rate equations might seem, in this particular case, the rate equation would have two stationary solutions, such that the asymptotic dynamics would strongly depend on the initial state of the system at time $t = 0$.

In the Jahn–Teller configuration, in contrast to the purely electronic model or the Anderson–Holstein molecule, no electronic level can be decoupled completely from a single electrode by a unitary transformation. As explicated above, only a certain subset of transitions can be decoupled, the others remain with finite transition rates. Since this property renders the decoupling paradigm for the Jahn–Teller molecule void at first sight, it restricts the current-blockade to the voltage regime below the first vibronic sideband, but in return allows to evaluate the model even in the regime where Eq. 8 is satisfied and the Anderson–Holstein model splits up.

III. TRANSPORT PROPERTIES

A. General Phenomenology

In the weak-coupling regime $\Gamma \ll k_{\mathrm{B}}T, \hbar\omega$, most transport calculations using rate equations show results, where the Coulomb-blockade physics of the electronic levels is augmented by a vibronic structure and the appearance of vibronic sidebands in the current–voltage profile.[18] Significant diversions from this picture only occur in the case of very weak electron–phonon coupling,[24] where the vibronic dynamics heat the molecule, or very strong coupling,[4] where the huge displacement of the oscillators' adiabatic potential causes an exponential suppression of

the low-bias current—the Franck–Condon blockade.

In the presence of two degenerate electronic levels being described by a master equation for the full reduced density matrix, we expect this paradigm to still hold true. The Coulomb-blockade physics of the electronic structure is enhanced by the coherent current blockade[16] due to the presence of the dark state. Depending on the ratio $U/\hbar\omega$, we shall observe vibronic sidebands in the form of peaks rather than steps on-top of the profile of the current blockade ($U > \hbar\omega$) or the current blockade modifying the first few vibronic sidebands ($\hbar\omega > U$). The numerical evaluation of the stationary current for the two generic molecular models shown in Figure 2 corroborates this reasoning. The Anderson–Holstein molecule complies well with this argument as the formation of the dark state is not influenced by the vibronic structure. By contrast, the inability of the Jahn–Teller molecule to completely decouple one electronic level shows up in the modification of the transport properties at the first vibronic sideband only.

The role of the Lamb-shift contributions is in general the same as in the purely electronic case, yielding an additional intra-dot tunneling Hamiltonian of the form of a pseudo-magnetic field $\boldsymbol{B}$, which connects the two degenerate states via virtual intermediate states in the electronic reservoirs. The x-components of these fields in the pseudo-Bloch equation for $\vec{S}^q$ are, due to the symmetry $\gamma_\alpha^{pq} = \gamma_\alpha^{qp}$,

$$B_\alpha^q(\mu_\alpha) = \sum_p \gamma_\alpha^{pq} \left[\mathcal{P}\!\int \frac{f(\varepsilon - \mu_\alpha)}{(p - q)\hbar\omega + U + eV_{\mathrm{g}} - \varepsilon} d\varepsilon \right.$$
$$\left. + \mathcal{P}\!\int \frac{1 - f(\varepsilon - \mu_\alpha)}{(q - p)\hbar\omega + eV_{\mathrm{g}} - \varepsilon} d\varepsilon \right]. \quad (10)$$

We assume the electronic bands of the leads to be wide enough to ensure $\mathcal{P}\!\int \frac{1}{\varepsilon} d\varepsilon \approx 0$. All summands vanish simultaneously at $eV_{\mathrm{g}} - \mu_\alpha = \frac{1}{2}U$, where, similarly to the purely electronic case, the current is completely blocked: $I = 0$.

Independently of U, there is a contribution of the vibronic excitations to the pseudo-magnetic fields, which
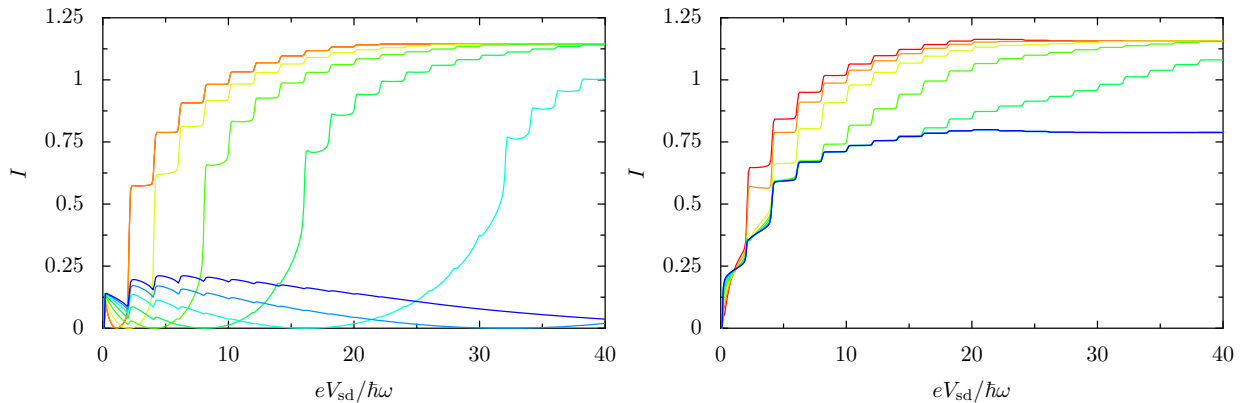
FIG. 2: (Color online): Stationary current as a function of the bias eV_{sd} for various values of $U/\hbar\omega = 1, 2, 4, 8, 16, 32, 64, 128$—red to blue curves. The electron–phonon coupling strenght is $\lambda = 1.1$, the tunnel coupling is $\mathbf{\Gamma} = (1, 1, 1, 2)$. (a) Anderson–Holstein molecule. For small $U/\hbar\omega$, the coherent current-blockade is only seen before the first vibronic sideband. For higher values of $U/\hbar\omega$, the sidebands appear as a peak-superstructure on the large-scale current-blockade. Since the current-blockade and the total inhibition of current flow at $eV_{sd} = U/2$ is the dominating feature of this dynamics, the vibronic sidebands become peaks thus rendering the appearance of negative differential conductance a generic property of this model. (b) Jahn–Teller molecule. The coherent phenomenology in the stationary current is limited to the regime before the first vibronic sideband, as due to the σ_z type electron–phonon coupling, the decoupling cannot be performed for all vibronic excitations of a given electronic level.

goes beyond the purely electronic model. A non-interacting molecule with $U = 0$, will still have finite pseudo-magnetic fields as the terms with $p \neq q$ in Equation (10) do not cancel but yield a contribution that is sharply peaked at the vibronic resonances. This causes slight derivations of the line shape in the differential conductance from the rate-equation result $\frac{d}{dV}I \propto \frac{d}{dV}f \propto f(1 - f)$, the derivative of the Fermi function.

B. Strong Electron–Phonon Coupling

Similarly to the rate-equation treatment, we expect the molecular models to show significant influence of the vibronic structure on the transport properties in the regime of strong electron–phonon coupling.[4,9] In Figure 3, we show the stationary current of the Anderson–Holstein model at intermediate electron–phonon coupling $\lambda = 1.1$ in contrast to strong coupling $\lambda = 4$, where the system is deep in the Franck–Condon blockade regime.

In Figure 3 (a), we see the suppression of the low-bias current due to the Franck–Condon blockade. The additional suppression of the stationary current at higher bias is not known from the rate-equation model and due to the intrinsic mechanism of the master equation with coherences. We have shown previously[16] and also in this paper that by identifying an exact dark state in the model, we can find the stationary state of the system. If we can find a state that can be populated easily but leaks only very little probability, this state is still a candidate to acquire much population in steady-state and apt to dominate the transport physics. Applying this to the large-bias regime of the Anderson–Holstein molecule in the Franck–Condon blockade yields an explanation for the observed effect. Assume a large charging energy of

several $\hbar\omega$ and bias and gate voltage chosen such that the singly occupied state is aligned slightly above the drain electrode and the doubly occupied state well below the Fermi level of the source electrode. Then the state $|\sigma, 0\rangle$ is almost dark because of the exponentially suppressed Franck–Condon matrix elements for the transition $|\sigma, 0\rangle \mapsto |0, 0\rangle$ at the drain. In the conventional rate-equation formalism this would not reduce the transparency of the device as one could occupy the second level and tunnel off to the drain by converting the large charging energy into vibronic excitations. In the coherent setting, however, we are allowed to decouple one electronic state from one electrode, and although we have up to now only decoupled one state from the drain electrode, we could easily decouple one from the source electrode; let this state be $|\bar{\sigma}\rangle$. The Franck–Condon blockade thus obstructs tunneling to the drain electrode, and the decoupling from the source electrode does not allow to doubly charge the device, hence reducing the conductance of the device drastically. As before, the Lamb-shift contributions help to regularize this picture, by transferring the charge from $|\sigma\rangle$ to $|\bar{\sigma}\rangle$, allowing a second electron to occupy the device and converting the charging energy to vibronic energy in the tunneling to the drain electrode. In this particular setting, the roles of source and drain electrode have been reversed in the game of decoupling and transferring charge via virtual intermediate state of the reservoirs compared to the low-bias regime.

C. Particular Phenomenology of Jahn–Teller molecules

The electron–phonon coupling of a Jahn–Teller molecule is proportional to σ_z in the electronic Hilbert
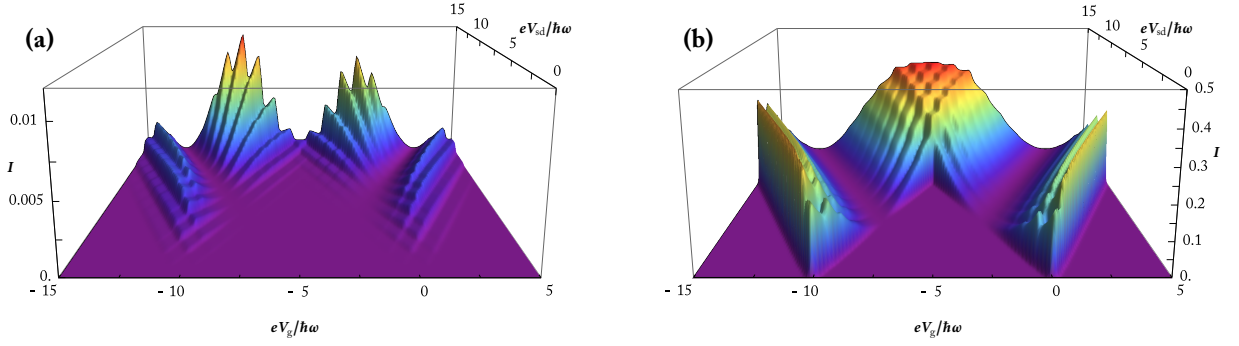
FIG. 3: (Color online): Stationary current of the Anderson–Holstein molecule in the Franck–Condon blockade regime for $\lambda = 4$ (a) and for intermediate coupling $\lambda = 1.1$ (b). Although the obvious effect of strong electron–phonon coupling is a suppression of the stationary current at the Coulomb-blockade line and the double-charging threshold, the current profile develops sharp spikes at larger bias. The parameters are $U = 10\hbar\omega$ and $\mathbf{\Gamma} = (1, 1, 1.5^2, 0)$.

space and thus breaks the rotational invariance of the molecular Hamiltonian, which we have exploited to understand the steady-state dynamics. We have already shown that this results in the inability to decouple an electronic level completely from one of the electrodes, thus obstructing the use of generic tunnel couplings. Looking closer at the quantitative properties of the master equation, the consequences can be seen in a number of effects.

The different directions of the shift of the adiabatic potentials implied by the polaron transformation introduce a sign dependence on certain rates in the master equation. In particular the rates γ_α^{pq}, will have different signs for $|p - q|$ being even or odd. When we encounter a situation, where the x-component of the pseudo-magnetic fields plays an important role in the dynamics, for example by transferring charge from a dark state into a conducting one, the structure of the Jahn–Teller molecule's electron–phonon coupling will cause a significant reduction of B_x and thus of the current restoring force. The consequence is, in comparison with the Anderson–Holstein molecule, a profile of the coherent current blockade, which hardly shows an influence of the Lamb shift at all, having a much higher contrast as is shown in Figure 4.

A second effect of the broken symmetry in the Jahn–Teller molecule is the ability to push the system into the parameter regime, where the Anderson–Holstein molecule would naturally split into two independent systems, that is, when the ratio $t_{\alpha\uparrow}/t_{\alpha\downarrow}$ is independent of the lead index α as given by Equation 8. The main difference between the two models is that Jahn–Teller molecules the pseudo-magnetic fields are non-zero. In this regime, the pseudo-Bloch equations for the model in a voltage regime
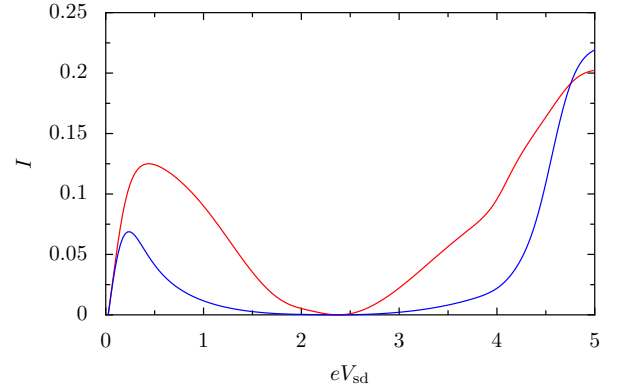

FIG. 4: Effects of small pseudo-magnetic field in the x-direction. Tunnel coupling $\mathbf{\Gamma} = (1, 1, 0, 1)$, zero gate voltage, Anderson–Holstein: red, Jahn–Teller: blue, $U = 2.35\hbar\omega$

before the first vibronic sideband is

$$\Gamma_{\mathrm{S}} p_0 - \frac{1}{2}\Gamma_{\mathrm{D}} p_1 - \frac{1}{2}\Gamma_{\mathrm{D}} S_z = B_x S_y$$

$$-\Gamma_{\mathrm{S}} p_0 + \frac{1}{2}\Gamma_{\mathrm{D}} p_1 + \frac{1}{2}\Gamma_{\mathrm{D}} S_z = 0$$

$$-\frac{1}{2}\Gamma_{\mathrm{D}} S_x + B_z S_y = 0$$

$$-\frac{1}{2}\Gamma_{\mathrm{D}} S_y + (B_x S_y - B_y S_x) = 0.$$

Because $B_x \neq 0$, this equation is *uniquely* solved with $\vec{S} = 0$. A completely vanishing pseudo-spin is not only the statement that the coherences of the stationary density matrix are evaluated zero but that also the steady-state populations of both electronic levels are equal. Such a result is unexpected insofar as it is independent of the ratio $\Gamma^\uparrow/\Gamma^\downarrow$, which in a rate-equation treatment would determine the pseudo-spin's z-component. Also, a vanishing pseudo-spin means that the reduced density matrix in the singly-charged sector is proportional to the unit matrix and invariant under rotations in the electronic Hilbert space.

IV. MODIFICATIONS OF THE BASIC MODEL

In this section, we shall discuss several extensions of our basic model of a single-molecule junction with orbital degeneracies, which are related to experimental issues such as not having exact degeneracy or single-mode reservoirs.

A. Slight Breaking of the Degeneracy

The requirement of strict degeneracy of the two orbitals is quite unphysical, when one takes into account all the physics of a single-molecule junction that we have neglected in the abstract model. However, the derivation of a master equation for the reduced density matrix requires strict degeneracy in order not to sacrifice the density matrix's coherences to the rotating-wave approximation. Although there have been some attempts in the literature to derive a proper master equation for this case via the, not necessarily positive, Bloch–Redfield equation,[11,15] we have shown in a previous work[16] how such an equation can be derived rigorously by treating the breaking of degeneracy as a perturbation.

Assume the degeneracy of the electronic system Hamiltonian $H_S = (\varepsilon_0 + eV_g)\sum_\sigma d_\sigma^\dagger d_\sigma$, or using the pseudo-spin notation $H = (\varepsilon_g + eV_g)\text{Id}$, is broken by $H_\Omega := \frac{1}{2}\Omega\sigma_z$, that is $H_\Omega = \frac{1}{2}\Omega(d_\uparrow^\dagger d_\uparrow - d_\downarrow^\dagger d_\downarrow)$ in second quantization. Assuming this perturbation to be a slight breaking of the degeneracy that will not destroy the coherences in the reduced density matrix implies the relation $\Omega \sim \Gamma \ll k_B T, \hbar\omega$. Following the derivation given in Ref. 16, we only have to add the Liouvillian $\mathcal{L}_\Omega = [H_\Omega, \cdot]$ to the master equation found for the degenerate, $\Omega = 0$, model. This term induces a second contribution to the Hamiltonian part of the master equation besides the Lamb shift; the splitting essentially adds to the z-component of the pseudo-magnetic field, but in contrast to the Lamb shift, Ω is a free parameter of the theory. Its influence on the steady-state transport properties of our single-molecule devices will be investigated in the next few sections.

1. Anderson–Holstein Molecules

As we have shown before, for intermediate electron–phonon coupling, the Anderson–Holstein molecule's behavior is a superposition of the phenomenology of the electronic levels and the vibronic sideband structure.

In the numerical evaluation of $I(eV_{sd})$ as a function of Ω in Figure 5 (a), the current suppression is lifted for larger splitting Ω, and the small vibronic peaks develop into well-defined steps of the current profile, which are typical for the rate-equation treatment. Due to different tunneling-induced pseudo-magnetic fields $\vec{B}^q$, for each vibronic excitation but constant splitting Ω, the lifting of the coherent structure and the recovery of the flat profile

is different for each sideband. In Figure 5 (a), the various vibronic sidebands emerge at different values of Ω.

2. Jahn–Teller Molecules

Due to the inability to decouple all vibronic excitations of a single electronic level from the drain electrode in the Jahn–Teller model, the coherent current blockade being the generic phenomenology of Anderson–Holstein molecules is in general only visible if the zero of the source's pseudo-magnetic field is at a voltage below the first vibronic sideband. In Figure 5 (b), we show the Ω-dependent stationary current at zero gate voltage for intermediate charging energy. As we have claimed, the current blockade is localized close to zero bias and vanishes quickly as the splitting Ω is increased. Since the zero of $\vec{B}_S$, where the current blockade is fully developed, is shifted towards higher voltages for large charging energy and therefore far beyond the first vibronic sideband, systems with larger Coulomb repulsion will not show any suppression at all.

For finite Ω, however, we can shift the zero of $\vec{B}_S$ so far that it moves below the first vibronic sideband allowing the vibronic ground state to become dark. We show our findings in Figure 6, where we plot the current suppression due to *finite* Ω. Figure 6 (a) shows the current profile for $eV_g = -\hbar\omega$ and varying splitting Ω. The dip in the stationary current for $\Omega \approx 0.6$ is due to the mentioned effect. Diagrams (b) and (c) show a complete current–voltage profile in the (eV_g, eV_{sd})-plane. For $\Omega = 0$ (b), the current suppression is absent for all voltages. For $\Omega = 0.6$ (c), on the contrary, there is a deep trough of suppressed current, slightly reminiscent of the phenomenology of the Anderson–Holstein molecule, but only for the first vibronic sideband and negative gate voltage.

3. General linear electron–phonon coupling

In the introduction, we have considered the general situation of linear electron–phonon couplings. For degenerate electronic systems, these can be always diagonalized leaving only the identity and the σ_z component of the electron–phonon coupling matrix in the electronic Hilbert space $\mathcal{H}_{el}$ $\Lambda = \lambda_0\text{Id} + \lambda_z\sigma_z$. Due to the polaron transformation, the system's electronic levels will acquire an energy difference proportional to $4\lambda_0\lambda_z$. The strictly degenerate theory, $\Omega = 0$, can only be applied to either the Anderson–Holstein model, $\lambda_z = 0$, or the Jahn–Teller model, $\lambda_0 = 0$. Using the concept of near-degeneracies, however, we can go beyond this sharp distinction and consider molecules with both λ_0 and λ_z being non-zero and include the splitting due to the polaron transformation as a near-degeneracy Ω. Such models are interesting, because the different electron–phonon coupling of the
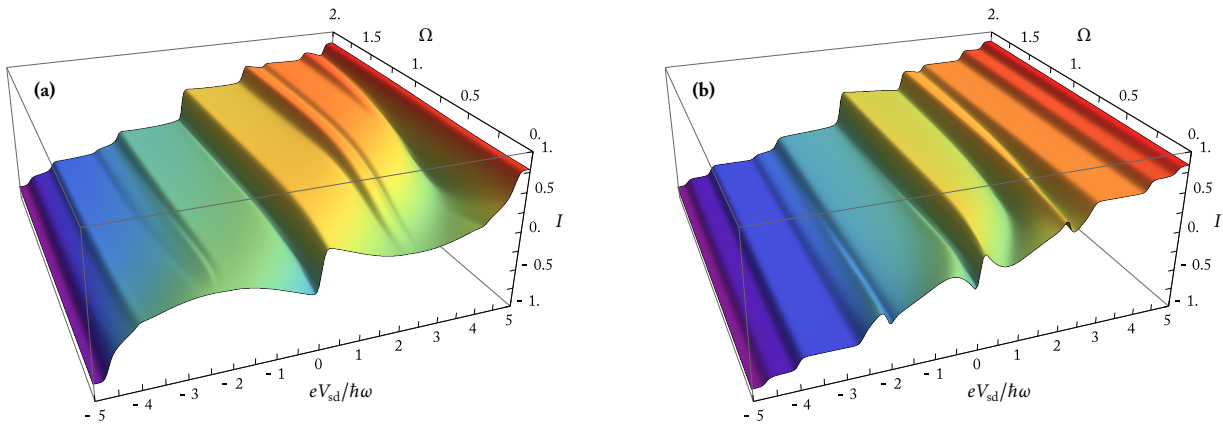
FIG. 5: Scan of Ω at $eV_{\mathrm{g}} = 0$, $eV_{\mathrm{sd}} \in [-5\,\hbar\omega, 5\,\hbar\omega]$, $U = 2.35\,\hbar\omega$, (a) Anderson–Holstein molecule with $\lambda = 1.1$, $\boldsymbol{\Gamma} = (1, 1.5^2, 1.5^2, 1)$. The splitting is not measured in units of $\hbar\omega$ but, due to the singular-coupling limit $\Omega \sim \Gamma$ in units of $\frac{2\pi}{\hbar}\nu_0$. (b) Jahn–Teller molecule for the same parameters.
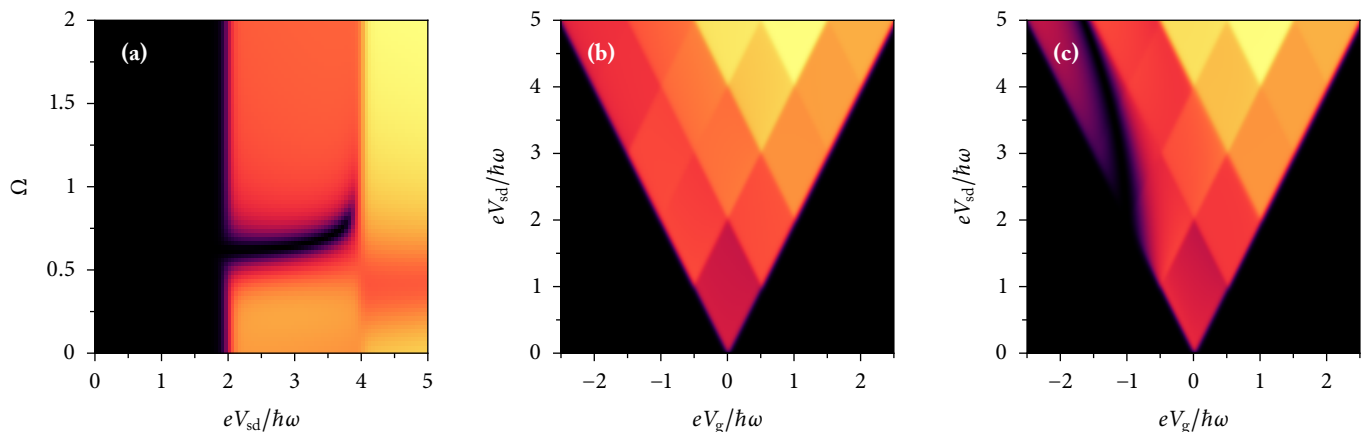

FIG. 6: (a) Scan of Ω for the Jahn–Teller molecule at $eV_{\mathrm{g}} = -\hbar\omega$, $\Gamma = (1.7^2, 1, 1.4^2, 1)$, $U = 10\,\hbar\omega$, $\lambda = 1.1$, and $k_{\mathrm{B}}T = 0.02\,\hbar\omega$. (b) stationary current for $\Omega = 0$, $eV_{\mathrm{sd}} \in [0, 5\,\hbar\omega]$, $eV_{\mathrm{g}} \in [-2.5\,\hbar\omega, 2.5\,\hbar\omega]$. (c) same plot, however, with $\Omega = 0.6$, where similarly to the Anderson–Holstein molecule, a trough in the stationary current due to the coherent blockade effect is visible.

system's levels amount to different Franck–Condon matrices, for example one level being weakly coupled, the other being in the Franck–Condon blockade regime.

B. Multi-Mode Reservoirs

In a number of recent publications, electronic transport through single molecules is realized by using suspended carbon nanotube quantum dots.[8,9] Following the experimental set-up used in Ref. 9, a top-gate attached to the suspended nanotube defines the central piece of it as a quantum dot, the outer pieces as electron supplies directly connected to the metallic source and drain electrodes, and all three regions being separated through mechanical deformations of the nanotube. The principal effect of the thus created tunnel barriers to the left and the right of the nanotube quantum dot is that we cannot, in general, assume the valley quantum number

of graphene to be conserved in tunneling anymore. If we denote the valley quantum number of the quantum dot region in accordance with the notation for degenerate orbitals used throughout this article by σ and the valley quantum number of the supplying nanotube electrodes by τ, the tunnel matrix elements acquire an additional index $\Gamma^{\sigma}_{\alpha\tau}$. Instead of formerly four, we now have eight tunnel matrix elements, and it is immediately clear from this number that the paradigm of electronic decoupling at the drain electrode, which we have established in the discussion of the Anderson–Holstein molecule, is no longer generically true for such systems. The reduction of the master equation to a rate equation in a suitably chosen basis of the electronic Hilbert space can, however, nonetheless be achieved. Let us consider the noninteracting retarded self-energy of the tunneling problem with respect to a single electrode, where we assume that
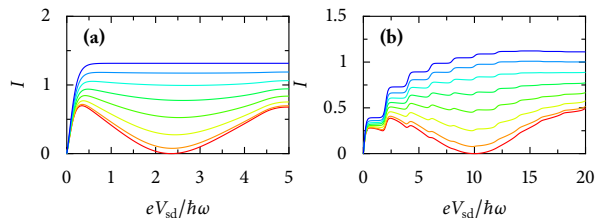
FIG. 7: (a) Two-mode reservoir interacting with a two-level quantum dot with $U = 2.35\,\hbar\omega$, $k_BT = 0.05\,\hbar\omega$. (b) Two-mode reservoir interacting with an Anderson–Holstein molecule. $U = 10\,\hbar\omega$, $k_BT = 0.05\,\hbar\omega$, and $\lambda_\uparrow = \lambda_\downarrow = 1.1$. The coupling to the left electrodes are equal and set to unity, and the ones to the right electrode are $t_{R\uparrow,\uparrow} = 1.4$, $t_{R\uparrow,\downarrow} = t_{R\downarrow,\uparrow} = 0$. The coupling $t_{R\downarrow,\downarrow}$ is scanned from 0 to 1.4 (red to blue curves) in order to increase the eigenvalues of Σ_R from $(\Sigma^-, \Sigma^+) = (0, 1.4)$, where the effect of the two-mode reservoir is absent, linearly to $(\Sigma^-, \Sigma^+) = (1.4, 1.4)$, where the coherent current blockade is gone.

the electrodes' distribution function is diagonal in τ,

$$\Sigma_\alpha \propto \begin{pmatrix} \sum_\tau \Gamma_{\alpha\tau}^\uparrow & \sum_\tau \gamma_{\alpha,\tau} \\ \sum_\tau \gamma_{\alpha,\tau} & \sum_\tau \Gamma_{\alpha\tau}^\downarrow \end{pmatrix}. \qquad (11)$$

This matrix is hermitian and can thus be diagonalized with its off-diagonals being zero. If we choose α to be the drain electrode, the master equation without the pseudo-magnetic fields is rendered a rate equation. But now there is no generic dark state and transport does not proceed via just one electronic levels but including both; however, in a manner known from rate-equation theory. Assume the eigenvalues of Σ_D are $\Sigma^+ \gg \Sigma^-$. Then the electronic system will accumulate more population in the eigenstate of Σ^- and its exit rate towards the drain electrode will determine the steady-state current. The pseudo-magnetic fields induce an intra-dot tunneling term, which pushes population from $|\downarrow\rangle$ to $|\uparrow\rangle$ and thus increases the steady-state current when the bias voltage is tuned away from the point $|B| = 0$. In Fig. 7, we show numerical results for this model, where we increase the smaller eigenvalue of Σ_D from zero, which corresponds to the situation found in single-mode reservoirs, to Σ^+, where the negative differential conductance structure has vanished, for in that case, both reservoir modes are coupled to the molecule equally well, and the drain's self-energy is proportional to the unit matrix.

The physical significance of this result is the following. The graphs in Fig. 7 (b) do resemble the current–voltage diagrams computed in Ref. 11. And indeed, the problem of electronic transport with ferromagnetic leads formally resembles our model as there it is the real electronic spin, which is present both in the electrodes and the quantum dot, but due to the ferromagnetic ordering not conserved in the tunneling. The primary influence of the presence of more than one electronic mode in the leads is the lifting of the strict current-blockade and the accompanying softening of the negative differential conductance at the vibronic sidebands.

V. CONCLUSION

The transition from the rate-equation physics of a single spin-degenerate quantum dot to a single-molecule junction is essentially the addition of inelastic transitions, which first of all cause vibronic sidebands. Only in certain regimes of the model's parameter space, additional vibronic physics like for instance the Franck–Condon blockade are visible. In the present article, we have proceeded in a similar manner to extend the master-equation theory for systems with orbital degeneracies from electronic levels to molecular models, where the main persistent phenomenology is the addition of vibronic sidebands to the generic current suppression due to the coherent interaction of degenerate or near degenerate electronic levels. With two instead of only one level, we have shown that already in the Hamiltonian, the decoupling paradigm, being the essential tool to understand the transport dynamics, is modified by the matrix structure of the tunnel amplitudes in the polaron picture. We have shown that in the strictly degenerate case, there are two generic models, which we have termend Anderson–Holstein and Jahn–Teller, with opposite phenomenology. While the Anderson–Holstein model complies well with the idea that an electron–phonon coupling simply adds the well-known vibronic physics to the steady-state dynamics of the electronic model, we have shown that the phenomenology of the Jahn–Teller model shows many different transport regimes. The main reason being the inability to completely decouple an electronic level from one electrode by unitary transformations of the degenerate orbitals. The decoupling can only be achieved for a certain subset of vibronic excitations, which significantly influences the steady-state properties of the transport model.

We have thoroughly discussed the phenomenology of the generic models in various parameter regimes both for the tunneling amplitudes and the electron–phonon coupling. In the last part of the paper, we have relaxed the requirement of strict degeneracy of the electronic orbitals and allowed for so-called near-degeneracies, whose influence on the transport properties of purely electronic systems we have already investigated in a previous publication. We have applied our results to the vibronic models and shown how electronic transport of both models was modified in these regimes. As a last step, we have turned to the electrodes and discussed the effect of multiple electronic modes in the leads. Our main result is a modification of the decoupling paradigm used in our theory. Although the coherent current blockade being generic for our models is lifted and, depending on the parameters, only slightly reduced by the presence of more than one electronic mode in the electrodes, applying unitary transformations in the space of the degenerate orbitals of the molecule again proves a suitable tool to reduce the master equation to a rate equation for specific voltages and thus understand its stationary solution intuitively

We are well aware that none of the models, we have

discussed so far, would be a complete and quantitative description for any experiment as the models are too abstract. However, we have shown that already our models show the generic phenomenology found for more complex systems, for example in Ref. 15, and that we can understand its physics on a very fundamental basis. We have shown how to bring the master equation into a form where its dynamics can be understood intuitively using basic principles already known from rate-equation theory. With our approach to the theory of electronic transport through single-molecule devices with orbital degeneracies we therefore provide a basis for future research in the physics of coherent interactions in sequential tunneling beyond the rate-equation approach.

Appendix A: Derivation of the Master Equation

Our aim is the study of the steady-state transport properties of the molecular models in the weak-coupling limit, which amounts to only consider sequential tunnel-

ing processes. To achieve this, we will derive a markovian master equation closely following Refs.[25–27]. This derivation, whose principal ideas have already been used by us in Ref. 16 is not contained in the extensive review by Timm,[10] but in our opinion it is the most intuitive and rigorous derivation, because it reduces the necessary assumptions by a large degree when compared to other approaches. The Hamiltonian of our problem is that of a system–bath interaction and has the general form

$$H^\xi = H_{\mathrm{S}} + H_{\mathrm{E}} + \xi H_{\mathrm{S\text{-}E}}. \tag{A1}$$

There is a finite-dimensional discrete system H_{S}, the single molecule, an infinite particle reservoir, the environment H_{E}, which in our model are the electronic leads, and a system–bath coupling $H_{\mathrm{S\text{-}E}}$, namely the tunneling Hamiltonian. The parameter ξ in front of $H_{\mathrm{S\text{-}E}}$ symbolizes the weak-coupling assumption. Later $\xi \to 0$ will be implied and, in order to obtain a non-trivial result, an asymptotic time scale will be chosen. The quantity of interest is the reduced density matrix of the system S, $\rho_{\mathrm{S}} := \mathrm{Tr}_{\mathrm{E}}(\rho)$. obtained by means of a projection operator $\mathcal{P}\rho := \mathrm{Tr}_{\mathrm{E}}(\rho) \otimes \rho_{\mathrm{E}} = \rho_{\mathrm{S}} \otimes \rho_{\mathrm{E}}$. Also $\mathcal{Q} := \mathrm{Id} - \mathcal{P}$. The environment's density matrix will be the equilibrium distribution, which for fermions is just the Fermi-distribution. The von Neumann equation $\dot\rho = -\imath[H^\xi, \rho] =: -\imath\mathcal{L}^\xi\rho$ is split into an equation for $\mathcal{P}\rho$ and one for $\mathcal{Q}\rho$ and integrated formally by using the variation-of-constants formula known from the theory of ordinary differential equations, where $\mathcal{L}_i$ refers to the Liouvillian with respect to H_i,

$$\rho_{\mathrm{S}}(t) = e^{-\imath\mathcal{L}_{\mathrm{S}}t}\rho_{\mathrm{S}}(0) - \xi^2 \int_0^t e^{-\imath\mathcal{L}_{\mathrm{S}}(t-s)} \left\{ \int_0^s \mathrm{Tr}_{\mathrm{E}}\left(\mathcal{L}_{\mathrm{S\text{-}E}}e^{-\imath\mathcal{L}^\xi(s-u)}\mathcal{L}_{\mathrm{S\text{-}E}}\rho_{\mathrm{E}}\right)\rho_{\mathrm{S}}(u)du \right\} ds. \tag{A2}$$

By choosing a factorized density matrix as the initial condition $\rho(0) = \mathcal{P}\rho(0)$, we implement the Born approximation and obtain the integral equation for the reduced density matrix *alone*. The substitution $s = u + v$ allows to pull the reduced density matrix out of the inner integral, change the bounds of integration, and move to the interaction picture with respect to the system Hamiltonian

$$\rho_{\mathrm{S}}^{\mathrm{I}}(t) = \rho_{\mathrm{S}}^{\mathrm{I}}(0) - \xi^2 \int_0^t e^{-\imath\mathcal{L}_{\mathrm{S}}s} \left\{ \int_0^{t-s} e^{\imath\mathcal{L}_{\mathrm{S}}v} \mathrm{Tr}_{\mathrm{E}}\left(\mathcal{L}_{\mathrm{S\text{-}E}}e^{-\imath\mathcal{L}^\xi v}\mathcal{L}_{\mathrm{S\text{-}E}}\rho_{\mathrm{E}}\right)dv \right\} e^{-\imath\mathcal{L}_{\mathrm{S}}s}\rho_{\mathrm{S}}^{\mathrm{I}}(s)\,ds. \tag{A3}$$

We aim at deriving a Markovian master equation for which we have to consider a time scale on which all memory effects are absent. This time scale is defined by the asymptotic time $\tau = \xi^2 t$, which is being held constant in the limiting process $\xi \to 0$, such that

$$\rho_{\mathrm{S}}^{\mathrm{I}}(\tau) = \rho_{\mathrm{S}}^{\mathrm{I}}(0) - \xi^2 \int_0^\tau e^{\imath\mathcal{L}_{\mathrm{S}}\frac{\sigma}{\xi^2}} \left\{ \int_0^{\frac{\tau-\sigma}{\xi^2}} e^{\imath\mathcal{L}_{\mathrm{S}}v} \mathrm{Tr}_{\mathrm{E}}\left(\mathcal{L}_{\mathrm{S\text{-}E}}e^{-\imath\mathcal{L}^\xi v}\mathcal{L}_{\mathrm{S\text{-}E}}\rho_{\mathrm{E}}\right)dv \right\} e^{-\imath\mathcal{L}_{\mathrm{S}}\frac{\sigma}{\xi^2}}\rho_{\mathrm{S}}^{\mathrm{I}}(s)\,d\sigma. \tag{A4}$$

Proceeding with the limit $\xi \to 0$, we find that the operator in curly brackets converges[27] to

$$\mathcal{D} := \int_0^\infty e^{\imath\mathcal{L}_{\mathrm{S}}v} \mathrm{Tr}_{\mathrm{E}}\left(\mathcal{L}_{\mathrm{S\text{-}E}}e^{-\imath(\mathcal{L}_{\mathrm{S}}+\mathcal{L}_{\mathrm{E}})v}\mathcal{L}_{\mathrm{S\text{-}E}}\rho_{\mathrm{E}}\right)dv, \tag{A5}$$

An expansion of the Liouvillians in terms of commutators yields the nested commutator structure well known from standard perturbative treatments of the problem.[10] The

action of the two exponential factors $\exp(\pm\imath\mathcal{L}_S\sigma/\xi^2)$ to the left and right of $\mathcal{D}$ is to produce the time average $\bar{\mathcal{D}}$ of the operator.[27] The Markovian master equation is thus

$$\dot{\rho}_S(\tau) = -\bar{\mathcal{D}}\rho_S(\tau), \qquad (A6)$$

whose explicit representation for the models discussed in this paper is given in Appendix B 1. In Refs. 25 and 27, one finds a very elegant argument, why the time average of $\mathcal{D}$, being an exact result in the limit $\xi \to 0$, yields the secular or rotating-wave approximation, which is usually applied to decouple the coherences between non-degenerate states from the respective populations in the reduced density matrix.

We compute the stationary current within the same framework and start from the general definition of the observable. The stationary current through lead α is

$$\langle I_\alpha \rangle = \mathrm{Tr}_{S+E}(I_\alpha \rho_{S+E}). \qquad (A7)$$

The quantum mechanical current operator for lead α is the time-derivative of the number operator of this electrode,[28]

$$I_\alpha = \frac{\imath e}{\hbar} \sum_{\boldsymbol{k}\sigma} t_{\alpha\sigma} c_{\boldsymbol{k}\alpha}^\dagger d_\sigma - \text{h.c.}, \qquad (A8)$$

which is the imaginary part of the operator $\sum_{\boldsymbol{k}\sigma} t_{\alpha\sigma} c_{\boldsymbol{k}\alpha}^\dagger d_\sigma$. The tunneling Hamiltonian H_T is the real part of this operator. We split the expectation value $\langle I_\alpha \rangle$ into two parts by inserting $\mathrm{Id} = \mathcal{P} + \mathcal{Q}$,

$$\langle I_\alpha \rangle = \mathrm{Tr}_{S+E}(I_\alpha \mathcal{P}\rho_{S+E}) + \mathrm{Tr}_{S+E}(I_\alpha \mathcal{Q}\rho_{S+E}). \qquad (A9)$$

The first term naturally vanishes, because $\mathcal{P}\rho = (\mathrm{Tr}_E \rho)\otimes \rho_E$, and the system–bath coupling has zero expectation value with respect to the equilibrium distribution of the electrodes. It is the projection onto the complement which is the interesting term. The time evolution of $\mathcal{Q}\rho_{S+E}$ is given by[29]

$$\mathcal{Q}\rho_{S+E}(t) = e^{-\imath\mathcal{Q}\mathcal{L}_{S+E}\mathcal{Q}t}\mathcal{Q}\rho_{S+E}(0)$$
$$- \imath \int_0^t ds\, e^{-\imath\mathcal{Q}\mathcal{L}_{S+E}\mathcal{Q}(t-s)}\mathcal{Q}\mathcal{L}_{S+E}\mathcal{P}\rho_{S+E}(s).$$

After integrating the defining equation for the current $I = -\dot{N}$ being the time derivative of the number operator of the respective electrode, we obtain an integral equation for the latter. We apply the same manipulations as before, using a factorized initial condition for ρ_{S+E}

that cancels the first term, and changing to the asymptotic Markovian time scale, which shifts the integration boundaries to infinity and takes the density matrix out of the integral. The Liouvillian $\mathcal{P}\mathcal{L}_{S+E}\mathcal{Q}$ acting on a factorized density matrix is $\xi\mathcal{L}_{S-E}$. The emerging formula is identical to the standard, perturbative derivation, where the factorization of the density matrix has to be put in by hand but only *after* certain manipulations have been applied to the formula. However, we now know that we can use the already obtained density matrix from Eq. (A6) and put it into the formula for the stationary current. An explicit formula in the basis of the single-molecule device is given in Appendix B 1.

Appendix B: Explicit Form of the Master-equation

1. Master equation

In this section, we give the explicit representation of the master equation (A6) for a two-level molecule with arbitrary Coulomb interaction U. The symbols used are defined by $p_0^q := |0,q\rangle\langle 0,q|$, $p_\sigma^q := |\sigma,q\rangle\langle\sigma,q|$, and $p_2^2 := |\uparrow\downarrow,q\rangle\langle\uparrow\downarrow,q|$, where the first entry specifies the charge state of the molecule and the second the number of excited quanta of the harmonic oscillator in the polaron picture. The electrons are fermions, which requires to choose a definition of the wavefunction of the doubly occupied state, $|2\rangle := |\uparrow\downarrow\rangle = d_\downarrow^\dagger d_\uparrow^\dagger |0\rangle$. The matrix elements of the molecular terms in the tunneling Hamiltonian therefore differ for having a neutral or a doubly occupied state.

$$\langle\uparrow\downarrow|\, t_{\alpha\downarrow}^* d_\downarrow^\dagger\,|\uparrow\rangle = t_{\alpha\downarrow}^* = \langle\downarrow|\, t_{\alpha\downarrow}^* d_\downarrow^\dagger\,|0\rangle$$
$$\langle\uparrow\downarrow|\, t_{\alpha\uparrow}^* d_\uparrow^\dagger\,|\downarrow\rangle = -t_{\alpha\downarrow}^* = -\langle\uparrow|\, t_{\alpha\uparrow}^* d_\uparrow^\dagger\,|0\rangle.$$

We also assume only real tunnel matrix elements and a wide-band limit of the electronic reservoirs, that is the density of states is energy independent and then set to unity for convenience. We define several shorthands: $t_{\alpha\sigma}^{pq}$ is the tunnel amplitude in the polaron picture $t_{\alpha\sigma}\langle q\,|\,e^{-\lambda_\sigma(b^\dagger-b)}\,|\,p\rangle$, with λ_σ incorporating the direction of the adiabatic potential's shift of the specific model. $\Gamma_{\alpha\sigma}^{pq} := |t_{\alpha\sigma}^{pq}|^2$, $\gamma_\alpha^{pq} := t_{\alpha\uparrow}^{qp} t_{\alpha\downarrow}^{\dagger pq} = t_{\alpha\downarrow}^{qp} t_{\alpha\uparrow}^{\dagger pq}$. A missing index on Γ or γ indicates that the sum over the respective index is implied. The symbol $\mathcal{P}\!\int$ indicates the principal value integral.

$$\dot{p}_0^q = -2\pi \sum_{\alpha,p} f_\alpha(\varepsilon_1^p - \varepsilon_0^q)\Gamma_\alpha^{pq} p_0^q + 2\pi \sum_{\alpha\nu,p} \left(1 - f_\alpha(\varepsilon_1^p - \varepsilon_0^q)\right)\left(\Gamma_{\alpha\nu}^{pq}\rho_\nu^p + \gamma_\alpha^{pq}\, 2\,\mathrm{Re}\,\rho_{\sigma\bar{\sigma}}^p\right) \qquad (B1)$$

$$\dot{p}_2^q = -2\pi \sum_{\alpha,p}(1 - f_\alpha(\varepsilon_2^q - \varepsilon_1^p))\Gamma_\alpha^{qp} p_2^q + 2\pi \sum_{\alpha\nu,p} f_\alpha(\varepsilon_2^q - \varepsilon_1^p)\left(\Gamma_{\alpha\nu}^{qp}\rho_\nu^p - \gamma_\alpha^{qp}\, 2\,\mathrm{Re}\,\rho_{\sigma\bar{\sigma}}^p\right) \tag{B2}$$

$$\dot{\rho}_\sigma^q = -2\pi \sum_{\alpha,p}(f_\alpha(\varepsilon_2^p - \varepsilon_1^q)\Gamma_{\alpha\sigma}^{pq} + (1 - f_\alpha(\varepsilon_1^q - \varepsilon_0^p))\Gamma_{\alpha\sigma}^{qp})\rho_\sigma^q - 2\pi \sum_{\alpha,p}(-f_\alpha(\varepsilon_2^p - \varepsilon_1^q)\gamma_\alpha^{pq} + (1 - f_\alpha(\varepsilon_1^q - \varepsilon_0^p))\gamma_\alpha^{qp})\,\mathrm{Re}\,\rho_{\sigma\bar{\sigma}}^q$$
$$+ 2\pi \sum_{\alpha,p}(f_\alpha(\varepsilon_1^q - \varepsilon_0^p)\Gamma_{\alpha\sigma}^{qp} p_0^p + (1 - f_\alpha(\varepsilon_2^p - \varepsilon_1^q))\Gamma_{\alpha\bar{\sigma}}^{pq} p_2^p) - 2\mathcal{P}\int d\varepsilon \left\{ \frac{f_\alpha(\varepsilon)}{\varepsilon_2^p - \varepsilon_1^q - \varepsilon}\gamma_\alpha^{pq} + \frac{1 - f_\alpha(\varepsilon)}{\varepsilon_1^q - \varepsilon_0^p - \varepsilon}\gamma_\alpha^{qp} \right\}\mathrm{Im}\,\rho_{\sigma\bar{\sigma}}^q \tag{B3}$$

$$\dot{\rho}_{\sigma\bar{\sigma}}^q = 2\pi \sum_{\alpha,p}\left(f_\alpha(\varepsilon_1^q - \varepsilon_0^p)\gamma_\alpha^{qp} p_0^p - (1 - f_\alpha(\varepsilon_2^p - \varepsilon_1^q))\gamma_\alpha^{pq} p_2^p\right)$$
$$- \pi \sum_{\alpha,p}\left[\left(-f_\alpha(\varepsilon_2^p - \varepsilon_1^q)\gamma_\alpha^{pq} + (1 - f_\alpha(\varepsilon_1^q - \varepsilon_0^p))\gamma_\alpha^{qp}\right)(\rho_\sigma^q + \rho_{\bar{\sigma}}^q) + \left(f_\alpha(\varepsilon_2^p - \varepsilon_1^q)\Gamma_\alpha^{pq} + (1 - f_\alpha(\varepsilon_1^q - \varepsilon_0^p))\Gamma_\alpha^{qp}\right)\rho_{\sigma\bar{\sigma}}^q\right]$$
$$- i\mathcal{P}\int d\varepsilon \left\{ \frac{f_\alpha(\varepsilon)}{\varepsilon_2^p - \varepsilon_1^q - \varepsilon}\left((\Gamma_{\alpha\sigma}^{pq} - \Gamma_{\alpha\bar{\sigma}}^{pq})\rho_{\sigma\bar{\sigma}}^q + \gamma_\alpha^{pq}(\rho_{\bar{\sigma}}^q - \rho_\sigma^q)\right) + \frac{1 - f_\alpha(\varepsilon)}{\varepsilon_1^q - \varepsilon_0^p - \varepsilon}\left((\Gamma_{\alpha\sigma}^{qp} - \Gamma_{\alpha\bar{\sigma}}^{qp})\rho_{\sigma\bar{\sigma}}^q + \gamma_\alpha^{qp}(\rho_{\bar{\sigma}}^q - \rho_\sigma^q)\right) \right\} \tag{B4}$$

Some cosmetic simplifications can be applied by noting that $\Gamma^{pq} = \Gamma^{qp}$ and abbreviating the Fermi factors $f_{\alpha1}^{pq} := f(\varepsilon_1^p - \varepsilon_0^q - \mu_\alpha)$ and $f_{\alpha2}^{pq} := f(\varepsilon_2^p - \varepsilon_1^q - \mu_\alpha) = f(\varepsilon_1^q + U - \varepsilon_0^p - \mu_\alpha)$. In the Anderson–Holstein case, $\lambda_\sigma = \lambda_{\bar{\sigma}}$, also $\gamma^{pq} = \gamma^{qp}$. The stationary current through lead α can either be computed using the formulae given in section A or derived from the above equations of motion by noting that this current is given by the α-contribution of the expression $\sum_p(\dot{p}_0^p - \dot{p}_2^p)$. Either way we find

$$\frac{1}{2\pi}\langle I_\alpha \rangle = \sum_{\sigma,p,q} f_{\alpha1}^{pq}\Gamma_\alpha^{pq} p_0^p - \sum_{\sigma,p,q}(1 - f_{\alpha2}^{qp})\Gamma_\alpha^{qp} p_2^p$$
$$- \sum_{\sigma,p,q}\left[(1 - f_{\alpha1}^{pq})\Gamma_{\alpha\sigma}^{pq} - f_{\alpha2}^{qp}\Gamma_{\alpha\bar{\sigma}}^{qp}\right]\rho_\sigma^p$$
$$- \sum_{p,q}\left[(1 - f_{\alpha1}^{pq})\gamma_\alpha^{pq} + f_{\alpha2}^{qp}\gamma_\alpha^{qp}\right] 2\,\mathrm{Re}\,\rho_{\sigma\bar{\sigma}}^p. \tag{B5}$$

2. Pseudo-Bloch representation

The master equation (A6) for degenerate two-level systems can be cast into a more intuitive form, since the electronic system admits the description by a pseudo-spin $\vec{S}$ for the singly charged part of the reduced density matrix. Due to the vibronic structure there is a pseudo-spin for every excited vibrational state $|\sigma; q\rangle$ there is an additional index $\vec{S}^q$. The components of the pseudo-spin are naturally defined by

$$\vec{S}^q := \left(\mathrm{Re}\,\rho_{\uparrow\downarrow}^q, \mathrm{Im}\,\rho_{\uparrow\downarrow}^q, \rho_{\uparrow\uparrow}^q - \rho_{\downarrow\downarrow}^q\right). \tag{B6}$$

Due to the possibility of changing the charge state, the modulus of this spin is not constant, and the trace of ρ, $p_1^q := \sum_\sigma \rho_{\sigma\sigma}^q$ as the zeroth component of the Pauli-matrix representation has to also to be included. Here, we give an explicit representation of the master equation in terms of the pseudo-spin $\vec{S}^q$ and the populations of the three charging states.

$$\dot{\vec{S}}^q = \pi \sum_{\alpha,p}\Big[2f_{\alpha1}^{qp} p_0^p \vec{n}_\alpha^{qp} + (f_{\alpha2}^{pq}\vec{n}_\alpha^{pq} - (1 - f_{\alpha1}^{qp})\vec{n}_\alpha^{qp})p_1^q$$
$$- 2(1 - f_{\alpha2}^{pq})\vec{n}_\alpha^{pq} p_2^p\Big] - \sum_\alpha \pi \left[f_{\alpha2}^{pq} + (1 - f_{\alpha1}^{qp})\right]\Gamma_\alpha^{qp}\vec{S}^q$$
$$- (\vec{B}_1^{pq} + \vec{B}_2^{qp}) \times \vec{S}^q. \tag{B7}$$

The pseudo-magnetization $\vec{n}_\alpha^{pq}$ is defined by the tunnel couplings,

$$\vec{n}_\alpha^{pq} := \left(2\gamma_\alpha^{pq}, 0, \Gamma_\sigma^{pq} - \Gamma_{\bar{\sigma}}^{pq}\right) \tag{B8}$$

The pseudo magnetic fields are defined by the principal value terms

$$\vec{B}_1^{pq} := \sum_\alpha \mathcal{P}\int \frac{f_\alpha(\varepsilon)}{\varepsilon_2^p - \varepsilon_1^q - \varepsilon}d\varepsilon\, \vec{n}_\alpha^{pq}, \tag{B9}$$

$$\vec{B}_2^{qp} := \sum_\alpha \mathcal{P}\int \frac{1 - f_\alpha(\varepsilon)}{\varepsilon_1^q - \varepsilon_0^p - \varepsilon}d\varepsilon\, \vec{n}_\alpha^{qp}. \tag{B10}$$

The equations for the populations are in matrix form

$$
\frac{d}{dt}\begin{pmatrix} p_0^q \\ p_1^q \\ p_2^q \end{pmatrix} = \pi \sum_{\alpha p} \begin{pmatrix} -2f_{\alpha 1}^{pq}\Gamma_\alpha^{pq} & (1-f_{\alpha 1}^{pq})\Gamma_\alpha^{pq} & 0 \\ 2f_{\alpha 1}^{qp}\Gamma_\alpha^{qp} & -f_{\alpha 2}^{pq}\Gamma_\alpha^{pq}-(1-f_{\alpha 1}^{qp})\Gamma_\alpha^{qp} & 2(1-f_{\alpha 2}^{pq})\Gamma_\alpha^{pq} \\ 0 & f_{\alpha 2}^{qp}\Gamma_\alpha^{qp} & -(1-f_{\alpha 2}^{qp})\Gamma_\alpha^{qp} \end{pmatrix} \begin{pmatrix} p_0^q \\ p_1^q \\ p_2^q \end{pmatrix}
$$
$$
+ \pi \sum_{\alpha p} \left\{ \begin{pmatrix} 1-f_{\alpha 1}^{pq} \\ 0 \\ 0 \end{pmatrix} \vec{n}_\alpha^{pq}\cdot\vec{S}^p + \begin{pmatrix} 0 \\ f_{\alpha 2}^{qp} \\ 0 \end{pmatrix} \vec{n}_\alpha^{qp}\cdot\vec{S}^p + \begin{pmatrix} 0 \\ -(1-f_{\alpha 1}^{qp}) \\ 0 \end{pmatrix} \vec{n}_\alpha^{qp}\cdot\vec{S}^q + \begin{pmatrix} 0 \\ 0 \\ -f_{\alpha 2}^{pq} \end{pmatrix} \vec{n}_\alpha^{pq}\cdot\vec{S}^q \right\}.
$$
(B11)

By considering the dynamics of the electronic levels only and neglecting any oscillator excitations, the summations over p cancels due to $\delta_{p,q}$ and we obtain equations similar in form to Ref. 11.

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[30] We shall use the term "master equation" as a synonym for master equation for the full reduced density matrix, in order to contrast this equation to the rate equation, which only concerns the density matrix's diagonal elements.